HYDROGEN STORAGE MATERIAL, METHOD FOR PRODUCING THE SAME, HYDROGEN STORAGE TANK, HYDROGEN STORAGE SYSTEM, AND FUEL CELL VEHICLE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a hydrogen storage material, a hydrogen storage tank, a hydrogen storage system, a fuel cell vehicle, and a method for producing the hydrogen storage material.

2. Description of the Related Art

Recently, to overcome growing global environment issues, hydrogen has received attention as a clean energy source. With this tendency, the development of technologies for producing, storing and applying hydrogen has been accelerated. In a hydrogen storage system using a hydrogen storage material, it is presently considered that a hydrogen storage alloy is the most practical hydrogen storage material. In the best-known $LaNi_5$-based hydrogen storage alloy, the hydrogen storage ratio is 1.4 % by weight at normal temperature and at a hydrogen pressure of 1 MPa. Even in a vanadium-based hydrogen storage alloy, which recently has attracted attention, the hydrogen storage ratio is 2.4 % by weight. Because of these facts, it is considered that the hydrogen storage capacity has not yet reached a practical level. As another hydrogen storage material, a carbon-based material containing carbon as a base material, such as graphite, activate charcoal, or carbon nano-tubes is known. However, graphite shows a hydrogen storage capacity only in rare cases. The hydrogen storage ratio of activate charcoal is less than 1 % by weight and that of carbon nano-tubes is considered to be 3 % by weight or less.

Assuming that a hydrogen storage tank containing a hydrogen storage material is used in a fuel cell vehicle, in order to attain a desired 500 km-cruising distance on a single charge of hydrogen, about 5-kg hydrogen storage capacity

would be required. However, none of the aforementioned hydrogen storage materials can satisfy this requirement. This may be because each of the hydrogen storage materials does not have a molecular structure suitable for storing hydrogen. For example, planar molecular layers of graphite, namely, graphenes, have an interlayer distance of about 0.34 nm, which is too narrow to store hydrogen. Accordingly, in order to store hydrogen, the interlayer distance of graphenes must be increased. As a structure to trap gas in the interlayer space of a planar layer structure, a planar structure formed of a mixture of small planar molecules is known (see Japanese Patent Application Laid-Open No. 2000-24495).

SUMMARY OF THE INVENTION

In the structure formed of a mixture of small planar molecules, the space between the parallel layers of the structure which is considered to store hydrogen in a largest amount is restricted by the size of the molecules used therein. As a result, it is not easy to attain a high hydrogen storage capacity. On the other hand, as is shown in the aforementioned patent publication, when planar molecules such as graphite and spherical molecules are alternately stacked to form a parallel layered structure, individual layers must be stacked one by one, so that such a manufacturing process is not practical. In this case, since the space between the graphite layers itself is not used for storing hydrogen, the storage amount per volume or weight is not high. Also, in the case where fullerene is used as the spherical molecule, since fullerene is more easily hydrogenated than planar-form carbon, it is hydrogenated during the storage of hydrogen. As a result, this case has problems in that the recovery amount of hydrogen decreases and the space for storing hydrogen is decreased.

The present invention was made in consideration of the above-described problems. It is an object of the present invention to provide a hydrogen storage material having a sufficient hydrogen storage capacity, a hydrogen storage tank, a hydrogen storage system, a fuel cell vehicle and a method for producing the

hydrogen storage material.

The first aspect of the present invention provides a hydrogen storage material comprising: a plurality of planar molecular layers stacked; and a particle being inserted into the planar molecular layers to define an interlayer distance between the planar molecular layers.

The second aspect of the present invention provides a method for producing a hydrogen storage material comprising: arranging a planar molecular layer material and a metal material at different places in a vacuum chamber, followed by sealing the chamber; and controlling the temperatures of the planar molecular layer material and the metal material, independently, to insert a metal atom constituting the metal material into planar molecular layers formed of the planar molecular layer material.

The third aspect of the present invention provides a hydrogen storage tank, comprising: a hydrogen storage material including a plurality of planar molecular layers stacked, and a particle being inserted into the planar molecular layers to define an interlayer distance between the planar molecular layers.

The fourth aspect of the present invention provides a hydrogen storage system, comprising: a hydrogen storage tank including a hydrogen storage material which has a plurality of planar molecular layers stacked, and a particle being inserted into the planar molecular layers to define an interlayer distance between the planar molecular layers.

The fifth aspect of the present invention provides a fuel cell vehicle, comprising: a hydrogen storage system comprising a hydrogen storage tank including a hydrogen storage material which has a plurality of planar molecular layers stacked, and a particle being inserted into the planar molecular layers to define an interlayer distance between the planar molecular layers.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described with reference to the accompanying drawings wherein;

FIG. 1 is a schematic view showing a structure of a hydrogen storage material according to the present invention;

FIG. 2 is a schematic view showing a method for producing the hydrogen storage material according to the present invention;

FIG. 3 is a graph showing the calculated hydrogen storage amount (by weight %) of a hydrogen storage material in Example 1 and the Comparative Example;

FIG. 4 is a graph showing the calculated hydrogen storage amount (by volume %) of a hydrogen storage material in the Example 1 and the Comparative Example;

FIG. 5 is a graph showing the calculated hydrogen storage amount (by weight %) of a hydrogen storage material in Example 2 and the Comparative Example;

FIG. 6 is a graph showing the calculated hydrogen storage amount (by volume %) of a hydrogen storage material in the Example 2 and the Comparative Example;

FIG. 7 is a cross-sectional view showing a hydrogen storage tank filled with a hydrogen storage material according to the present invention;

FIG. 8 is a schematic view showing a hydrogen storage system using a hydrogen storage tank according to the present invention; and

FIG. 9 is a schematic view showing a fuel cell vehicle using a hydrogen storage system according to the present invention.

DETAILED DESCRIPTIONS OF THE PREFERRED EMBODIMENT

A hydrogen storage material, a method for producing the hydrogen storage material, a hydrogen storage tank, a hydrogen storage system, and a fuel cell vehicle according to the present invention will now be explained in detail with reference to the embodiments shown in the drawings.

(Hydrogen storage material)

As shown in FIG. 1, a hydrogen storage material according to the present invention includes a plurality of stacked planar molecular layers 1 and particles 2, which are inserted between the molecular layers 1 and increase the interlayer distance between the planer molecular layers 1. The particles 2 are chemically bound to the layers while being inserted between the molecular layers 1.

The planar molecular layer 1 is primarily formed of carbon such as graphene constituting graphite. Note that it is possible for the planar molecular layer 1 to contain a metal element in the molecule. The metal element may be selected from scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), aluminium (Al), potassium (K), rubidium (Rb), and cesium (Cs).

The particle 2 is selected from alkaline metal atoms such as potassium, rubidium, and cesium. By inserting such a particle 2 between planar molecular layers 1, the interlayer distance between graphite layers increases, so that hydrogen can be stored in the interlayer space between the graphite layers.

(Method for producing hydrogen storage material)

(Example 1)

In this example, an alkaline metal element is inserted between graphene layers by a vapor reaction method. This method is performed in accordance with the following steps i) and ii).

i) As shown in FIG. 2, arranging an alkaline metal and graphite as a planar molecular layer material at different places in a vacuum chamber, namely, a glass tube 3, followed by sealing the tube.

ii) Controlling the temperatures of the alkaline metal and graphite, independently, to insert the alkaline metal into graphite. When potassium is used as an alkaline metal, gaseous potassium is brought into contact with graphite, by increasing the temperature of graphite to 500°C or more and controlling the difference in temperature between potassium and graphite at 150°C or more, thereby causing an insertion reaction to produce a hydrogen storage material

having a potassium as an interlayer compound.

By placing the hydrogen storage material thus produced in hydrogen gas under pressure of about 5 to 10 MPa, the hydrogen storage material stores hydrogen into the interlayers thereof.

Note that the interlayer distance of the hydrogen storage material is measured usually by X-ray diffraction (XRD) or transmission electron microscopy (TEM). The interlayer distance of the graphite layers having an alkaline metal element (potassium) inserted therein and further storing hydrogen therein was about 0.85 nm, as measured by XRD.

Also, when a compound having cesium (Cs) serving as an alkaline metal between layers was formed in the same manner, the interlayer distance of graphite layers having hydrogen stored therein was about 0.81 nm. Note that an element and a compound other than an alkaline metal may be inserted.

When no hydrogen is stored to graphite having alkaline metal atoms inserted therein, the interlayer distance is about 0.5 to 0.6 nm. This is because, the alkaline metal atoms form a single layer between graphite layers, as shown in FIG. 1. In other words, this is because a unit of graphene - alkaline metal atom - graphene is repeated to form a graphite intercalation compound.

However, when hydrogen is inserted between graphite layers, alkaline metal atoms form a plurality of layers between the graphite layers. More specifically, a plurality of alkaline metal atoms are arranged, for example, graphene - alkaline metal atom - alkaline metal atom - graphene, in the direction perpendicular to the planar direction of graphene. As a result, the interlayer distance can exceed 0.8 nm.

The calculation results of hydrogen storage amounts according to the Example 1 will be shown below. This calculation was based on the Monte Carlo method. This is a probabilistic method using a random number for arranging molecules under a probabilistic rule and is frequently used for simulation of a system under a thermodynamic equivalent state. In this embodiment, the calculation was made assuming that the intermolecular force (potential) between

carbon atoms, that is, a secondary six-membered ring of carbons (graphene), and a hydrogen molecule, was 2.9 kJ/mol in agreement with experimental results.

FIG. 3 is a graph showing the hydrogen storage amount (% by weight) versus the interlayer distance of graphite at a temperature of 20°C and a pressure of 10MPa. In FIG. 3, the point indicated by the arrow A shows the calculated interlayer distance of graphite only, and it was found that hydrogen is not stored at all. In FIG. 3, a region enclosed by an oval figure indicated by the arrow B shows the calculated hydrogen storage amounts with respect to the structure corresponding to the Example 1. From the figure, it is found that the hydrogen storage capacity is exhibited after the interlayer distance increases and reaches 0.8 nm. The hydrogen storage capacity (% by weight) further increases up to about 6 % by weight with an increase of the interlayer distance, however, the storage amount per unit volume decreases as shown in FIG. 4. The carbonaceous hydrogen storage material has a small specific weight. Because of this, when a structural element containing the hydrogen storage material is arranged in a limited space such as a vehicle, the storage amount per unit volume also becomes an important factor for evaluating its storage capacity. In consideration of these factors, the most suitable interlayer distance becomes 0.8 to 1.2 nm in this embodiment.

(Example 2)

When a foreign element is inserted into graphene of graphite, the number of electrons within graphene changes, increasing the absorbability. In the Example 2, a metal element was inserted as the foreign element into graphene in addition to the constitution of the Example 1, thereby increasing the potential between hydrogen and graphene to 5 kJ/mol, which is about 1.7 times as high as that of the Example 1. The amount (obtained through calculation) of hydrogen stored by the hydrogen storage material according to this example is shown in FIGs. 5 and 6. More specifically, FIG. 5 is a graph showing the hydrogen storage amount in terms of % by weight, indicating that hydrogen is stored at an

interlayer distance of 0.8 nm or more, in the same as in the Example 1. When the interlayer distance reaches 1.2 nm or more, the storage amount per volume decreases. From these facts, the most suitable interlayer distance in the Example 2 is 0.8 to 1.2 nm, and more preferably, 1.0 to 1.2 nm.

(Comparative Example)

The point indicated by the arrow A in FIGs. 3 to 6 shows the amount (obtained through calculation) of hydrogen stored by a general graphite. As is apparent from the figure, hydrogen is not absorbed at all.

As is explained in the Examples 1 and 2, and the Comparative Example, the structure formed of graphite constituting a plurality of planar molecular layers (graphenes) and an alkaline metal inserted between planar molecular layers makes it possible to realize a highly stable hydrogen storage material having a sufficient hydrogen storage space and to be used suitably in a vehicle.

In the Examples 1 and 2 mentioned above, the particle to be inserted in planar molecular layers is an alkaline metal atom, however, an alkaline metal molecule may be inserted.

It is particularly preferable that the particle be chemically bound to a planar molecular layer (graphene in the Examples 1 and 2). It is also preferable that the planar molecular layer be formed primarily of carbon.

Furthermore, as is apparent from FIGs. 3 to 6, the interlayer distance between the planer molecular layers having hydrogen stored therein is preferably 0.8 to 1.2 nm.

Furthermore, it is preferable that the alkaline metal atom serving as a particle insert be at least one of potassium, rubidium, and cesium.

In the Example 2 mentioned above, a foreign element, particularly, a metal element, is inserted into graphene, thereby increasing the potential between hydrogen and graphene to 5 kJ/mol, which is about 1.7 times as high as that of the Example 1. From this, it is preferable that a metal element be contained in a

molecule of the planar molecular layer. The metal element is preferably any one of scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), aluminium (Al), potassium (K), rubidium (Rb), and cesium (Cs).

A method for producing a hydrogen storage material includes steps of arranging a planar molecular layer material and an alkaline metal material at different places in a vacuum chamber such as a glass tube, followed by sealing the chamber; and controlling the temperatures of the planar molecular layer material and the alkaline metal material, independently, to insert a metal atom constituting the alkaline metal material into the planar molecular layers formed of the planar molecular layer material. By virtue of the process, it is possible to easily and reliably produce a highly stable hydrogen storage material having a large hydrogen storage capacity per unit volume or unit weight.

(Hydrogen storage tank)

An embodiment of a hydrogen storage tank having a hydrogen storage material according to the present invention placed therein will be explained with reference to FIG. 7.

In the hydrogen storage tank 10 according to this embodiment, a tank main body 11 formed of a metal, which has a strength to withstand an inner pressure of 10 MPa or more, is filled with a hydrogen storage material 12 produced in the Example 1 or 2. The tank main body 11 has an inlet/outlet 13 for loading and unloading hydrogen. The inlet/outlet 13 is equipped with a tank valve 14.

Since the hydrogen storage material 12 of the present invention is used in the hydrogen storage tank 10, a light-weight hydrogen storage tank 10 capable of storing a large amount of hydrogen can be realized.

In this embodiment, the hydrogen storage material 12 may be introduced in the tank main body 11 either as it is or after it has been appropriately processed into a solid or a thin film form. Furthermore, if necessary, a filter 14A may be

provided to prevent leakage of the hydrogen storage material 12 from the tank. The hydrogen storage tank 10 may be installed in the fuel cell system or hydrogen engine system of a vehicle.

(Hydrogen storage system)

Next, the structure of a hydrogen storage system 20 having the hydrogen storage tank 10 applied thereto will be explained with reference to FIG. 8.

As shown in FIG. 8, the hydrogen storage system 20 is equipped with a temperature control apparatus 15 along the periphery of the tank main body 11 of the hydrogen storage tank 10, for controlling the temperature of the hydrogen storage tank 10 at a predetermined temperature. To the inlet/outlet 13 of the hydrogen storage tank 10, a pressure control apparatus 16 is connected. To the pressure control apparatus 16, a hydrogen suction port 17 and a hydrogen discharge port 18 are further connected communicably by way of pipes 19A and 19B, respectively. In the hydrogen storage system 20, hydrogen is supplied from the hydrogen suction port 17 to the tank main body 11 by way of the pressure control apparatus 16 and the tank valve 14, and is stored by the hydrogen storage material 12. When hydrogen stored in the tank main body 11 is taken out, hydrogen is controlled to be guided toward the hydrogen discharge port 18 through the pipe 19B via the tank valve 14 and the pressure control apparatus 16.

By the use of the hydrogen storage material 12 in the hydrogen storage tank 10 of the present invention, the hydrogen storage system 20 storing a large amount of hydrogen can be realized.

(Fuel cell vehicle)

FIG. 9 shows a fuel cell vehicle 30 having the hydrogen storage system 20 installed therein. The fuel cell vehicle 30 includes the hydrogen storage system 20 arranged in the front portion of a vehicle body 31, a fuel cell stack 21 arranged in the rear portion of the vehicle body 31, and a hydrogen delivering tube 22 connecting the hydrogen storage system 20 and the fuel cell stack 21.

In the fuel cell vehicle 30 according to the embodiment, since the hydrogen storage material 12 charged in the hydrogen storage tank 10 has a large hydrogen storage capacity per unit volume or unit weight, it is possible to prevent the entire weight of the hydrogen storage system 20 from being increased. Use of the hydrogen storage system 20 of the present invention makes it possible to realize the fuel cell vehicle 30 capable of storing a sufficient amount of hydrogen to attain a long-distance drive.

The entire content of a Japanese Patent Application No. P2003-039956 with a filing date of February 18, 2003 is herein incorporated by reference.

Although the invention has been described above by reference to certain embodiments of the invention, the invention is not limited to the embodiments described above will occur to these skilled in the art, in light of the teachings. The scope of the invention is defined with reference to the following claims.